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Investigation of Structural, Spectral, Optical and Thermal Properties in Grown L-Cystein Doped Bis Thiourea Zinc Acetate (L-Btza)

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Abstract: *The nonlinear optical single crystal of L-cystein doped bisthiourea zinc acetate (BTZA) was grown successfully by slow evaporation technique using water as solvent at room temperature. The influence of amino acid L-cystein on the lattice parameters of the grown crystal was determined by X-ray diffraction studies. The quality of the grown crystal was examined by scanning electron microscopy (SEM).The optical transparency was determined by UV-visible and Photoluminescence spectroscopy. The thermal behavior of the grown crystal was investigated by DTA and TGA analysis. The presence of functional group was studied using FTIR spectra. The second harmonic generation (SHG) of BTZA was confirmed the nonlinear property of the crystal by Kurtz powder technique.*

Keywords: *Crystal Growth, L-BTZA.*

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I. Introduction

Non linear optical frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology [1]. The growth and characterization of pure BTZA is reported by Niji Abraham and V S John et al, IOSR Journal of Applied Physics[2]. In the field of non linear crystal ,amino acids play a vital role as they exhibit natural chiral properties and crystallize in the noncentrosymmetric space group,which are an essential criterion for NLOapplications.[3].The growth and characterization of lithium chloride,cd2+,L-Proline doped BTZA crystals had also been reported by J.Thomas Joseph Prakash,L.Ruby Nirmala Spectrochimica Acta Part A:Molecular and Biomolecular Spectroscopy 97(2012) 673-677,M.Lydia Caroline ,S.Vasudevan Current Applied Physics 9(2009)1054-1061,J.Felicita Vimala,J.Thomas Joseph Prakash Spectrochimica Acta Part A:Molecular and Biomolecular Spectroscopy 107(2013) 371-376. L-Cystein the smallest naturally occurring aminoacid with a thiol group,offers a high degree of chirality due to the presence of three different functional groups[4].It has Zwitter ionic state in aqueous solution as well as in solid state.[5] The present Investigation deals with the effect of L-cystein on Bis Thiourea Zinc Acetate.

II. Experimental Details

Pure BTZA salt was synthesized by mixing zinc acetate and thiourea in the stiometric ratio 1:2 in double distilled water. The dopant L-cystein was added to the supersaturated solution of BTZA in the concentration of 2 wt% and stirred at a constant speed for six hours to attain homogeneity throughout the volume. The solution was filtered and kept for evaporation at room temperature. Good quality transparent crystals were harvested within a period of 20 days.

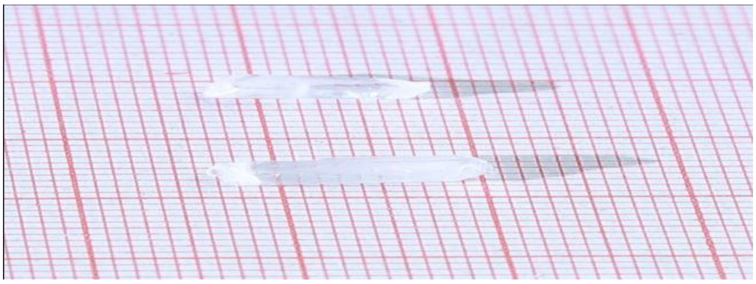

Fig 1: Photograph of L- BTZA single crystal

III. Results And Discussion

3.1 Single crystal XRD

The cell parameters of pure and L-Cystein doped BTZA crystals were carried out by single crystal XRD technique using Bruker Kappa Apex II diffractometer.The determined lattice parameters of pure and L-Cystein doped BTZA crystals are tabulated in table.Both the pure and the doped BTZA crystals are belong to the monoclinic system but there are variations in lattice parameters.The change in lattice parameters confirms the presence of L-Cystein in BTZA crystal.

Table 1

Chemical formula	BTZA	L-cystein doped
Cell Parameters	a = 7.1270 A˚ b = 17.7232 A˚ c = 11.1827 A˚	a = 7.1302(5) A b = 17.7091(15)A c = 11.1665(9) A
Volume	1375.79(12) A3	1373.00(19) A^3
Molecular Weight	335.7	335.70
System	Monoclinic	Monoclinic
Space group	P21/n	P21/n

The unit cell dimensions of L-cystein doped BTZA has been compared with the pure BTZA crystal which is shown in table 1.

3.2 Powder XRD

The powder diffraction patterns of pure and L-cystein doped BTZA is shown in fig :2, In the doped crystal the diffraction peaks becomes more intense due to the incorporation of L-cystein in to the lattice.

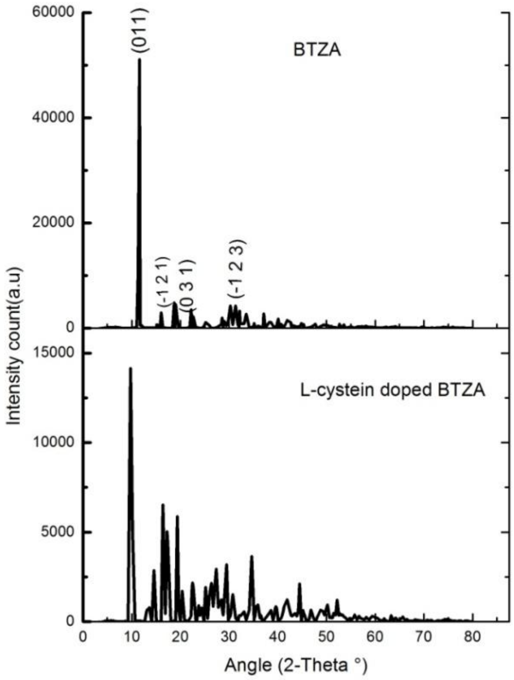

Fig 2: Powder XRD pattern of pure and doped BTZA

3.3 **Scanning Electron Microscopy**

The surface morphology of samples were analyzed with a scanning electron microscope JEOL MODEL JSM-6390LV, operating at 15 kV. The SEM photographs of the pure and doped BTZA are shown in fig 3.

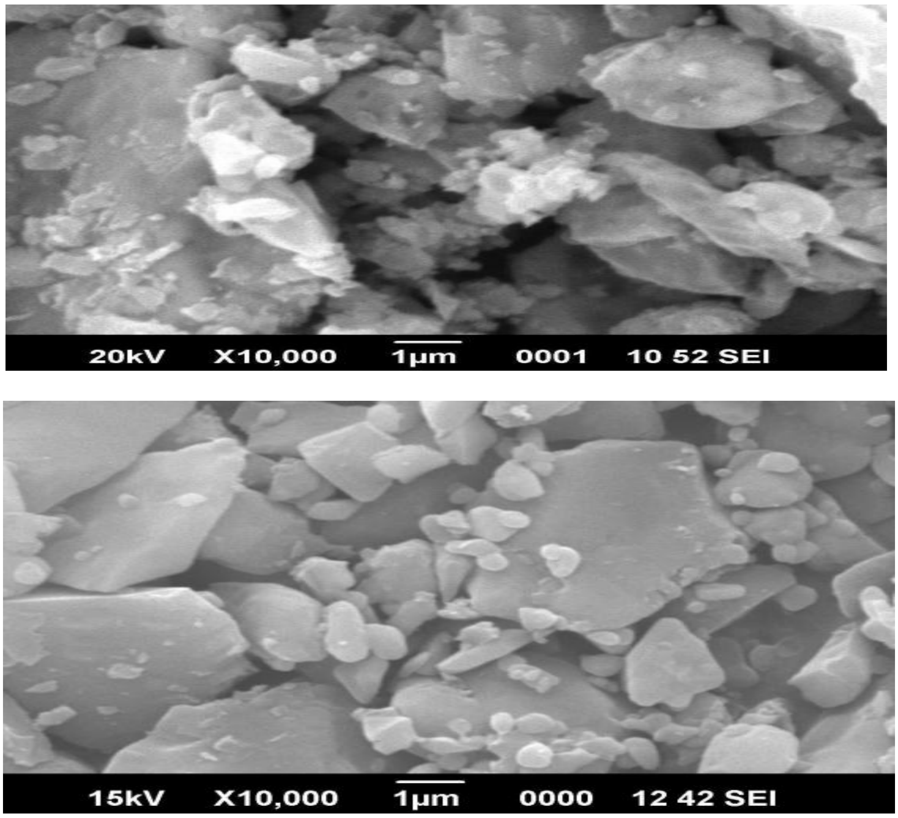

Fig 3: SEM images of Pure and doped BTZA crystal

From the photograph it can be concluded that the surface of the doped crystal is smooth compared to the pure sample which confirms that it can add more molecules to grow it to a large crystal.[9]

3.**4** **U V –Vis Spectroscopy**

The optical absorbance was recorded from uv visible in the wavelength range of 200-1200 nm using UV–Visible spectrophotometer (Varian,Cary 5000) . The thickness of the sample used for measurement was 2mm.The optical absorbance spectra of pure and doped crystals are shown in the fig.The lower cut off wavelength of L cystein doped BTZA is 300 nm which is lower compared to pure BTZA.From the Fig 4 it is clear that the optical transmission of L cystein doped BTZA in the visible region is higher than that for pure BTZA crystals. It is an added advantage in the field of optoelectronic applications [11].

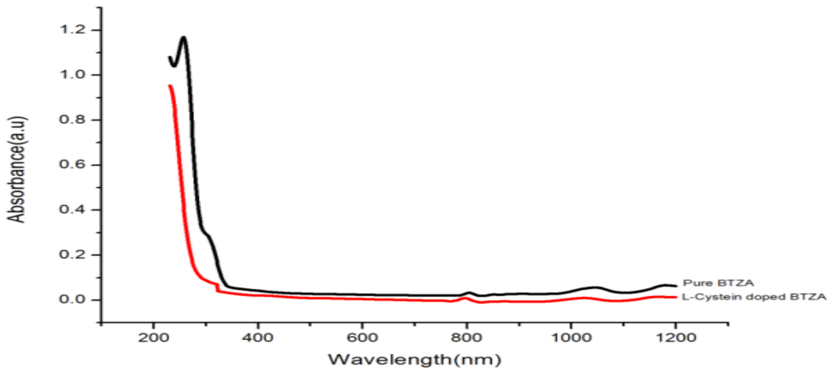

Fig 4: UV-Vis spectrum of pure and doped BTZA

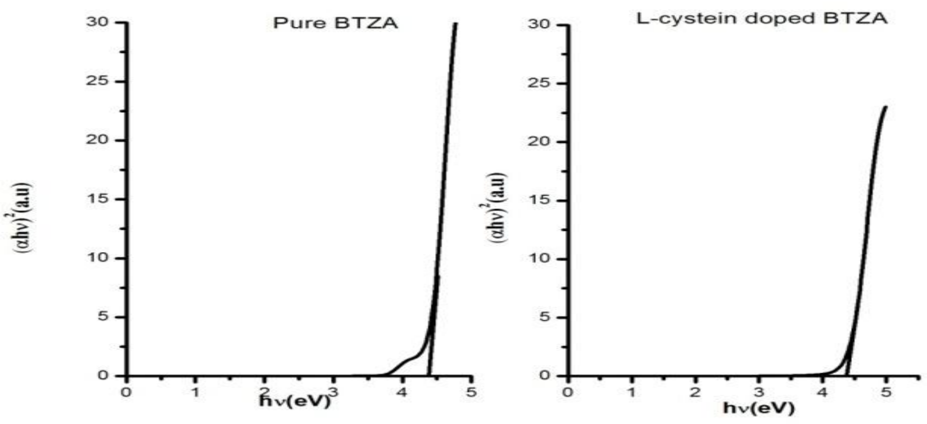

Fig 5: (αhν)2 versus photon energy (hν) of pure and doped BTZA

The value the bandgap was obtained using the relation $\alpha h\nu = A\,(h\nu\text{-}Eg)^{1/2}$ [3] where A is a constant, E_g the optical band gap ,h the Planck's constant .The graphs of (αhν)2 versus photon energy (hν) of pure and doped BTZA samples are shown in fig 5 .From the graphs the optical bandgap of pure and doped BTZA is estimated as 4.3 eV and 4.2eV respectively. It can be seen that band gap value decreased in the doped sample.

3.5 Photoluminescence

The photoluminescence (PL) spectrum of the pure and doped samples were recorded by fluorescence spectrometer, Perkin Elmer-LS 55, using an excitation wavelength of 275 nm is shown in the Fig 6. The Photoluminescence studies were carried to evaluate lower concentration of defects and transitional band gaps [4].The impurity on absorption of light gives rise to a bound excited state from which it returns to its ground state abiding in the analysis of colour centre creation mechanism[8].

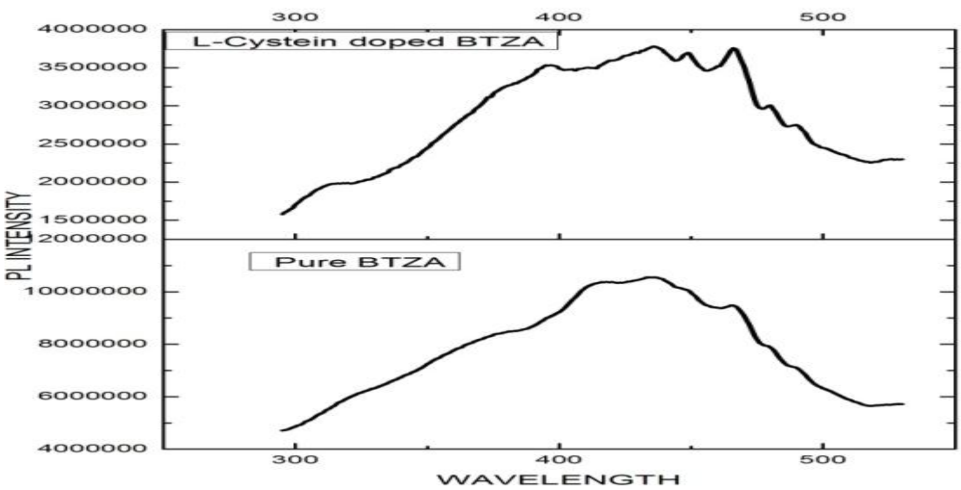

Fig 6: Photoluminescence spectrum of pure and doped BTZA

The sharp PL intensity confirms low transitional band gaps and high optical quality of doped BTZA crystal substantiating it for NLO applications [2].

3.6 Thermal studies

Thermal behavior of the pure and doped samples were analyzed by thermo gravimetric analyzer (TGA) and differential thermal analyzer (DTA) using Perkin Elmer STA 6000, heating from ambient to 700 °_C at a rate 10 °C/min is shown in fig 7. There is no weight loss below 160°C due to the absence of water in the crystal structure. In L-Cystein doped BTZA the major weight loss of about 74% takes place in the region 160°C to 300°C but in pure BTZA the major weight loss of about 57% takes place in the region 187^{o} C to 280^{o}C . The weight loss may be due to decomposition of the compound and organic compound evaporation and liberation of volatile substance like sulphurdioxide[6]. In pure BTZA the melting point is at 187.48 ^{o} C which is shifted to 189.30 o C when doped with 2 wt% of L-Cystein.

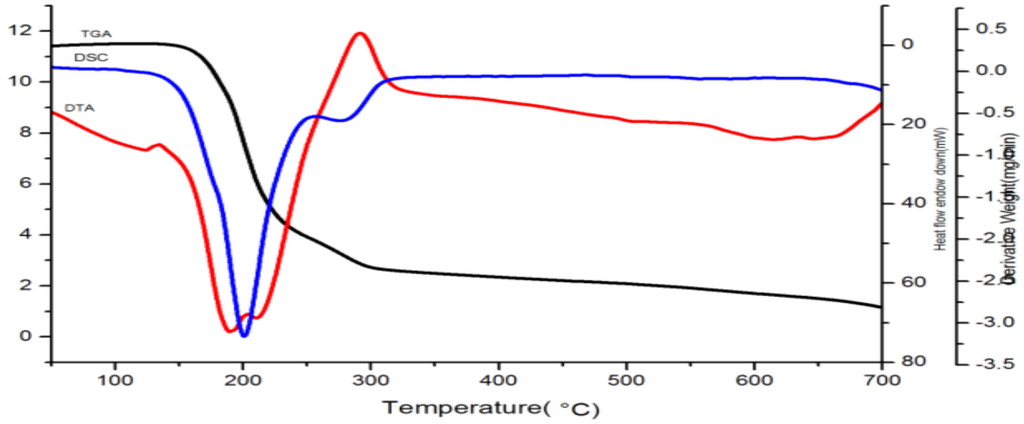

Fig 7: TG/DTA/DSC curves of pure and doped BTZA

3.7 NLO studies

The SHG efficiency of the grown crystal was determined using Kurtz and Perry method. A Q-switched mode locked Nd-YAG laser was used to generate about 1.13 mJ/pulse at the 1064 nm fundamental radiation. The input laser beam with pulse duration 10 ns and frequency repetition 10 Hz is passed through the micro crystalline powdered sample packed in a capillary tube. The efficiency of the sample was compared with the micro crystalline powder of KDP as the reference material. The second harmonic generation of the crystals was confirmed by bride green emission (532 nm) from the specimen. It was collected in a photomultiplier tube and finally measured on the storage oscilloscope (CRO) as output voltage. The efficiency of the L- cystein doped BTZA was found to be 1.6 times that of pure BTZA.

3.8 FTIR

Fourier transform infrared (FTIR) spectra of the pure and L- cystein doped BTZA were recorded by FTIR spectrophotometer (Thermo Nicolet, Avatar 370) in the range 4000 to 400cm-1 by KBr pellet technique and the spectra is shown in fig 8.The observed bonds along with their vibrational assignments were tabulated in Table 2.

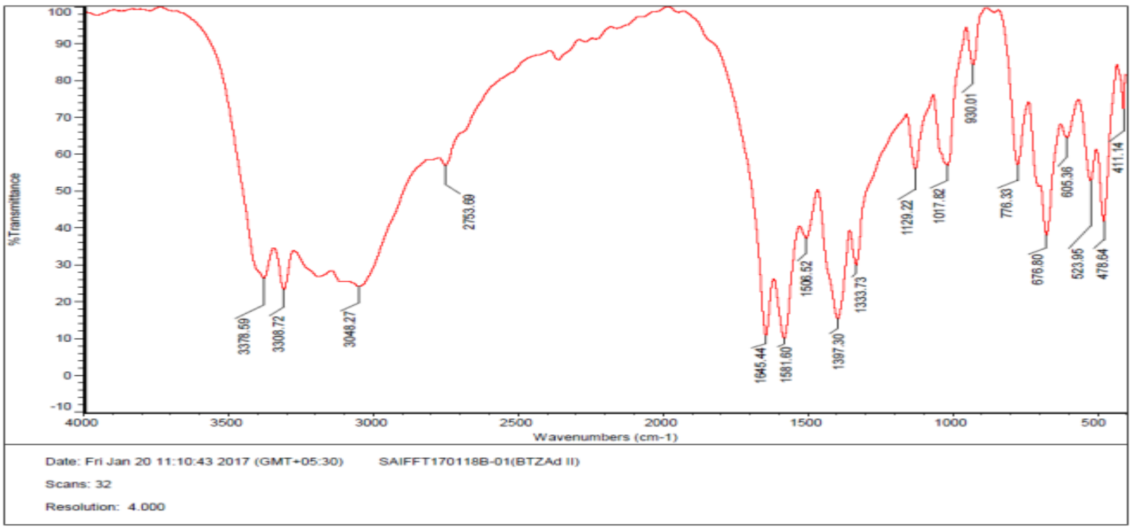

Fig 8:FT-IR spectrum of doped BTZA crystal

Table 2

BTZA cm^{-1} (reported [17])	BTZA cm^{-1}	L-Cystein doped BTZA cm^{-1}	Assignment
487	478	478.64	S-C-N symmetric bending
777	776	776.33	C=S symmetric stretching
1135	1129	1129.33	C=S symmetric stretching
1403	1396	1397.30	C=S asymmetric stretching
1582	1581	1581.60	NH2 bending
3375	3379	3378.59	NH2 stretching

IV. Conclusion

Good quality single crystal of L-cystein doped BTZA was grown by slow evaporation technique under room temperature. Grown crystals were characterized and compared with pure BTZA. Evaluation of lattice parameters confirm the dopents in to the lattice of the undoped BTZA crystal using single crystal XRD. Comparison study of Optical transmission confirms the improved quality of the doped crystals for NLO application. The photoluminescence studies of the doped sample confirms the quality of the crystals for photonic device applications. TGA and DTA analysis has revealed that thermal stability of doped BTZA is high compared to pure BTZA.. The functional groups were verified using FTIR analysis. SHG conversion efficiency makes the crystal a latent material for NLO application.

Acknowledgements

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